Support to Mars 2020 Participating Scientist Activities

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- **Goal:** Assemble databases of spectroscopic features for martian analog samples under martian-like conditions to support interpretation of data acquired by the SuperCam and SHERLOC instruments onboard the NASA Mars 2020 Perseverance rover.
- **Tasks:**

1. Preparation of martian analog samples.

2. UV irradiation processing of the martian analog samples under martian-like conditions.

3. Characterization of the martian analog samples before and after UV irradiation with instruments analogous to SuperCam and SHERLOC.

- **First Year Milestones:**

In order to put together a laboratory dataset to enable more accurate interpretation of the possible organics detected by the SHERLOC instrument in association with sulfates, we prepared and characterized Jezero analog samples composed of magnesium sulfate doped with various aromatic organic compounds, and we used them to perform detectability tests with instruments analogous to SuperCam and SHERLOC. Specifically:

1. 13 abiotic organo-sulfate analogs and 13 biotic organo-sulfate analogs were prepared. The abiotic organics include: the carboxylic acids phthalic acid, mellitic acid, and benzoic acid; the PAHs naphthalene, benzo[a]pyrene, 9-methylanthracene, coronene, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 1-naphthol and 2-naphthol; a synthetic analog for the meteoritic insoluble organic matter (IOM); the benzothiophenes 1-benzothiophene and dibenzothiophene. The biotic organics include: the amino acids L-phenylalanine, L-tyrosine, L-tryptophan; the nucleic acid components uracil, ATP (adenosine 5’-triphosphate), AMP (adenosine 5’-monophosphate), thymine, cytosine, adenosine, UMP (uridine 5’-monophosphate), adenine, guanine; the pigments porphyrin I, β-carotene, and melanin (two different melanins were synthesized in the lab, one containing nitrogen and the other without nitrogen). Samples were prepared by equilibrium adsorption of 1 wt% organic molecules on magnesium sulfate heptahydrate [MgSO4·7(H2O)].

2. UV irradiation experiments were performed for mellitic acid, phthalic acid, benzopyrene, 2,6-dihydroxynaphthalene, and uracil, both pure and adsorbed on Mg-sulfate.

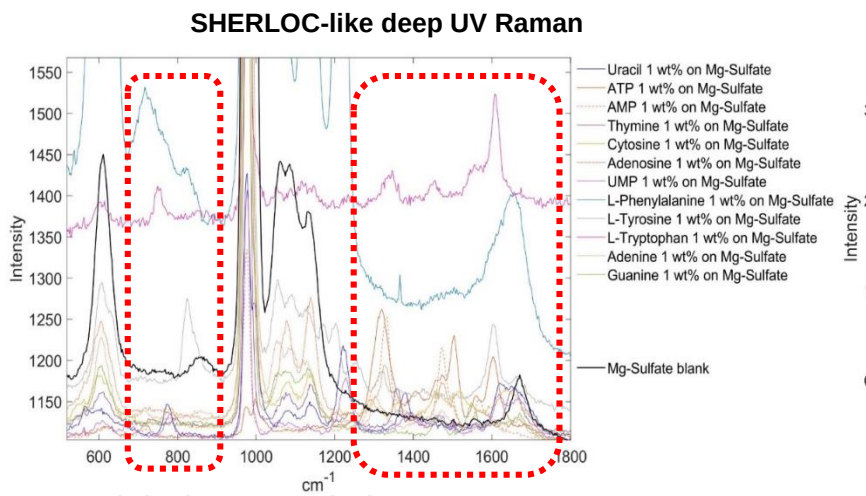
3. Samples were characterized with SHERLOC analog instruments, i.e. the ACRONM instrument located at NASA-JSC and the SHERLOC Brassboard instrument located at JPL, and SuperCam analog instruments, i.e. SimulCam, an instrument located at University of Valladolid (which is analog to the Raman part of SuperCam) and the Bruker VERTEX 70v interferometer available in the Arcetri Astrobiology Lab for VISIR characterization.

Highlights (papers in preparation):

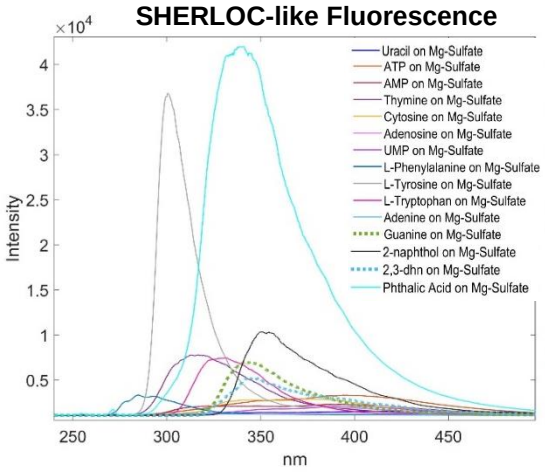
- SHERLOC deep UV Raman is the most diagnostic technique for organics identification because of the variability of molecular bands and distinctive patterns, which make easier to distinguish the specific molecular structures, but due to low organics abundance, in most of the cases only fluorescence has been observed which is much more sensitive. The problem of fluorescence, though, is that it is not very specific to molecular structures, but just gives indication of the general molecular classes.
- This lab work indicates that having co-located SHERLOC-SuperCam measurements might narrow down the range of molecules by looking at additional evidence for presence of organics such as:

1. Background variations in the SuperCam Raman, which depend on the specific organic molecule present in the sample due to a combination of organics luminescensce properties and grain size effects (which ultimately also depend on the specific organics since different organic molecules cause different ways of crystallization of Mg-Sulfate resulting in different grain sizes);
2. Variation of the intensity of the main Raman sulfate peak, which also appears to be dependent on the specific organic molecule present in the sample due to a combination of organics luminescensce properties and grain size effects;
3. Presence of weak organics bands in the SuperCam VISIR.

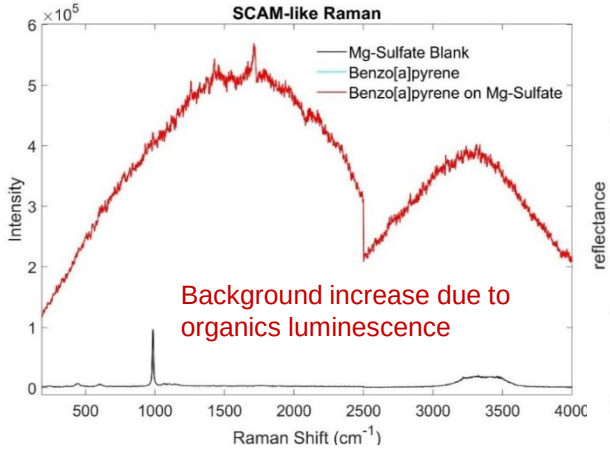
- Mg-Sulfate appears to be photoprotective, which is consistent with detection of possible organics in association with sulfates on Mars.



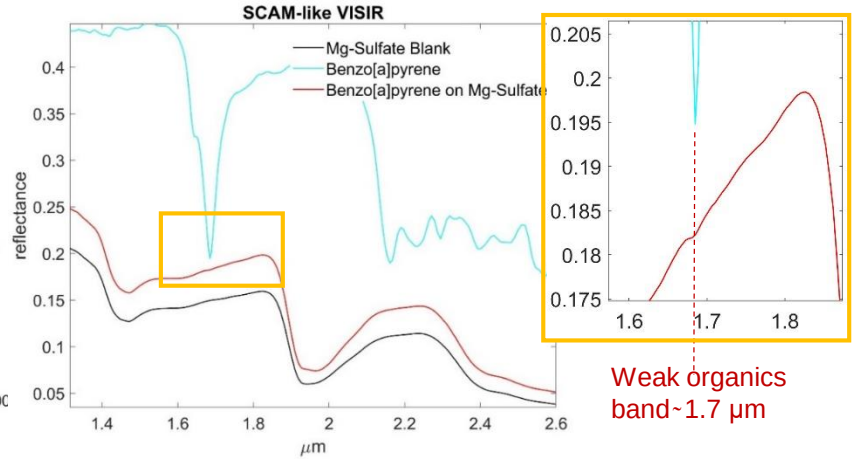
Distinctive patterns in deep UV Raman



Fluorescence is not very specific to molecular structures

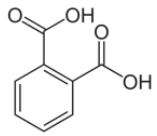


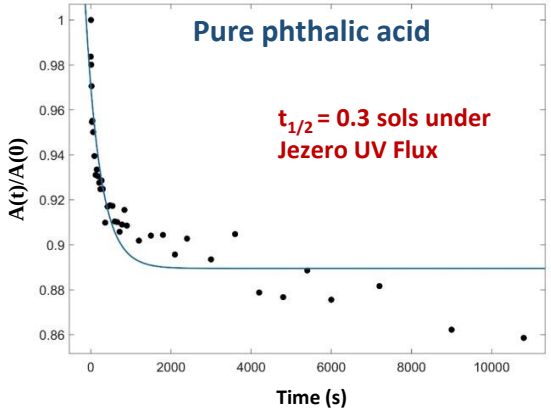
Background increase due to organics luminescence



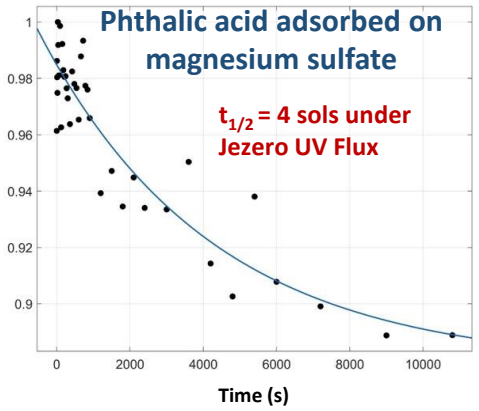
Weak organics band~1.7 μm

Degradation kinetics for the band at 1273 cm^{-1} (C-O stretch)





$t_{1/2}$ = 0.3 sols under Jezero UV Flux



$t_{1/2}$ = 4 sols under Jezero UV Flux

Dissemination of Results:

- **Invited talk at 109° Congresso Nazionale SIF 2023**, Dipartimento di Fisica dell'Università di Salerno (Italy), Sep 2023. Oral presentation: “The search for life on Mars”.
- **Mars 2020 Science Team Meeting 2023**, Paris (France), June 2023. Oral presentation: “Co-located SHERLOC-SCAM Measurements for Astrobiology”.
- **Biennial European Astrobiology Conference (BEACON) 2023**, La Palma Island (Canary Islands, Spain), May 2023. Oral presentation: “Inspecting the astrobiological relevance of samples collected at Jezero Crater on Mars by the NASA Mars 2020 Perseverance rover for future return to Earth”.
- **Invited talk at the Mars Sample Return 2nd Italian Workshop**, 25 October 2022, entitled: “The INAF Contribution to Mars 2020 Science: Inspecting the Astrobiological Relevance of Samples Collected at Jezero”.
- **Lunar and Planetary Science Conference 2023**, The Woodlands (USA), March 2023. Oral presentation: “Laboratory Investigations of Spectroscopic Features for Organo-Sulfate Complexes to Support Organics Identification in the Samples Analyzed by the Mars 2020 Perseverance Rover and Inspect the Astrobiological Relevance of the Samples to Be Returned to Earth”.
- **XVIII Congresso Nazionale di Scienze Planetarie 2023**, Perugia (Italy), Feb 2023. Oral presentation: “Detectability of Aromatic Organics in Sulfates by the Mars 2020 Perseverance Rover”.